

**FORMATION OF CARBONATES IN ALLAN HILLS 84001 BY IMPACT METASOMATISM: COOKING WITH GAS.** R. P. Harvey, Department of Geological Sciences, Case Western Reserve University, Cleveland OH 44106-7216, USA (rph@po.cwru.edu).

**Introduction:** The possibility that the carbonates in ALH 84001 were formed by the process of impact metasomatism was first put forth in Harvey and McSween (1996) ([1], hereafter called H&M). This short paper appeared roughly one month prior to that of McKay et al. (1996) where specific features of ALH 84001 were suggested to be the result of biological activity on ancient Mars [2]. In the media frenzy following that announcement, and subsequent scientific research, H&M was often cited as a counterpoint to the McKay groups hypothesis; often this was done as if it were the flag of a “resistance movement,” rather than as a part of the complex ALH 84001 puzzle. The purpose of this abstract is to explain the impact metasomatism hypothesis in greater detail than that early paper allowed, and offer an assessment of its validity in view of subsequent research.

**Impact Metasomatism Hypothesis, Restated:** H&M suggested that the carbonates found in ALH 84001 formed when an anhydrous CO<sub>2</sub> fluid, heated and mobilized by an impact, was flushed through impact-produced fractures of the original orthopyroxene cumulate lithology. This CO<sub>2</sub> fluid would initially be very hot and cool rapidly, with the whole event over in a period of minutes or seconds. During the first moments, when temperatures and pressures were at a maximum, reactions would occur between the high temperature fluid and the mafic components of the target lithology, enriching the fluid in Mg, Fe, and Ca. Immediate (a few seconds later) cooling of this fluid would induce precipitation of the carbonates as observed. H&M used the term impact metasomatism to describe this scenario, based on its similarity to mechanisms suggested for scrubbing CO<sub>2</sub> out of the ancient martian atmosphere [3,4]. The plausibility of impact metasomatism as a mechanism producing ALH 84001 carbonates was based on many lines of evidence, as follows.

**Mineralogical and Textural Considerations:** Most researchers agree that carbonate is found exclusively within the fractured zones of ALH 84001. While some have suggested that several distinct types of carbonate exist, evidence for this is sketchy in that all are space-filling or coat fracture surfaces and are compositionally indistinguishable. Indeed, the “type-specimen” carbonate has a circular or semi-circular habit in thin-section and on fracture surfaces, with a distinct pattern of compositional changes from core to rim, and all carbonates, regardless of setting, show a recognizable part of this pattern. This observation led H&M to the common belief that all carbonate in ALH 84001 originated from a single event. This also implies that carbonates grew sequentially from core to rim, nucleating from point sources, suggesting kinetic control of crystallization and possible time-sequence information.

While most research on fracture zone phases has centered on carbonate, the presence and absence of other phases is important to note. Chrome spinels form ubiquitous trains of crushed grains that characterize the maximum mechanical offset occurring during impact (on a scale of several mm in some cases). Maskelynite is also found preferentially associated with fracture zones and sometimes intimately intermixed with carbonate. While this has sug-

gested to some that carbonate forms by replacement of maskelynite [5,6], it cannot be that simple; the Fe/Mg composition of the carbonates requires a source for these cations, and no aluminous byproducts have been identified. Olivine with distinctive amoeboid grain shapes is another phase found exclusively within crushed zones. Finally, the expected products of hydrous alteration of ultramafic rocks, such as chlorite, serpentine, or similar phases, are for all intents and purposes, absent; only a few isolated sub-micrometer-sized grains have been identified, and it is not clear that they are contemporaneous with carbonate formation [7]. These findings argue for carbonate formation during a single, anhydrous event associated with a fluid percolating through fracture zones in ALH 84001.

H&M reported that the extreme “core” of carbonate growths was an Fe,Mg-rich calcite, intermixed with an ankeritic (50% Ca, 50% Mg,Fe) carbonate. This ankerite was in turn intermixed with the Fe-rich end-member of the relatively Ca-rich magnesite-siderite carbonates most commonly observed. While some specific compositions had been observed in terrestrial rocks, the suite as a whole has no known counterparts. Unfortunately the initial description of this in H&M was termed a “three-carbonate assemblage,” when it more accurately should have been considered a sequence of two component mixtures. That’s how the assemblage was treated when carbonate geothermometry was applied, yielding temperatures of 685°C (calcite-ankerite) and 660°C (ankerite-siderite) [8]. These temperatures were in remarkable agreement with the previously observed correspondence between magnesite-siderite compositions and the Ca-rich border of the 700°C magnesite-siderite stability field [9].

**Carbonate-producing Reactions:** In the simplest possible scenario, ALH 84001 carbonates would be produced from components derived solely from the host ultramafic mineralogy. Unfortunately, reactions that produce carbonate and other non-hydrous products from ultramafic rocks are not well studied; most of the literature concerns reactions with a hydrous fluid. However, some reactions are known in both natural and experimental settings, and provide insight into possible ALH 84001 carbonate formation mechanisms. Most notable are reactions that occur between ultramafic minerals and fluids with X<sub>CO<sub>2</sub></sub> higher than 0.85. Two that are of direct importance are:

- $2 \text{ forsterite} + 2 \text{ CO}_2 = 2 \text{ magnesite and 1 enstatite}$
- $1 \text{ enstatite} + 2 \text{ CO}_2 = 2 \text{ magnesite} + 2 \text{ quartz}$

Terrestrial studies predict these reactions will occur in sequence at about 660° and 620° respectively, at pressures between 3.5 and 5 kbar (or about 0.5 GPa) [10–12]. Several features of these reactions coincide well with what is observed in ALH 84001. The pressures are reasonable in the context of an impact event (mechanical twinning of pyroxene and conversion of plagioclase to maskelynite typically require 30 GPa or more), and the temperatures are suggestive. Furthermore, these reactions predict a mineralogical sequence that can be readily observed in ALH 84001. Olivine exhibiting reaction textures is sur-

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rounded by enstatite and associated with space-filling carbonate. In addition, spaces between carbonate growths are often filled with silica. One interesting point not noted in H&M, however, is that while the interstitial silica requires that the reactions proceed toward production of that phase and carbonate, the olivine textures could be the product of de-carbonation of preexisting carbonate.

**Microphases and Microtextures:** H&M suggested that the typical grain size of ALH 84001 carbonate was somewhat smaller than 1  $\mu\text{m}$ ; while some carbonate areas showed crystal faces and compositional homogeneity on the 1–10- $\mu\text{m}$  scale, plots of carbonate analyses showed linear mixing trends between calcite-ankerite and ankerite-siderite compositions. Following that lead, TEM and FE-SEM studies were conducted to explore carbonate mineralogy at the submicrometer scale. These studies confirmed a complex texture at submicrometer scales and revealed evidence for the mechanical and thermal effects of shock. Several observations best made sense in terms of gas-phase reactions at temperatures above ambient. For example, the magnetite assemblage observed throughout the carbonate included a variety of morphologies, some with specific crystalline defects typically associated with high-temperature vapor-phase growth [13]. These same crystals often had a rigorous epitaxial relationship to the carbonate substrate, indicating sufficient free surface energy during magnetite crystallization to allow cation mobility (i.e., elevated temperatures) [14]. These and other observations suggest temperatures of at least a few hundred degrees C either during carbonate crystallization or during alteration of preexisting carbonate [14,15]. These reactions could have occurred during the last moments of a metasomatic impact event, or during subsequent, lower energy impact events.

**Trace-Element and Isotopic Considerations:** Trace-element studies strongly suggested metasomatic reactions between ALH 84001 and an invasive fluid [16]. The isotopic composition of ALH 84001 carbonates has been more extensively studied, with interesting if more controversial results. Early studies of ALH 84001 leachates showed enrichments in  $^{13}\text{C}$  and  $^{18}\text{O}$  that were consistent with either high or low temperatures of formation; in general, low-temperature, aqueous scenarios for carbonate formation were favored [17]. However, H&M argued that this interpretation was soft for several reasons. First,  $^{13}\text{C}$  enrichments cannot unambiguously indicate a formation temperature without assuming a fluid composition, given the enriched nature of the martian atmosphere as a whole. Second, studies of natural impact-produced carbonates intermixed with mafic impact glasses show that isotopic disequilibrium between these phases is the norm, even though peak temperatures in excess of 1200°C must have been reached [4].

*In situ* studies of ALH 84001 carbonate using ion microprobe techniques produced equally polarized viewpoints. One study established that O isotopes within the observed sequential Mg,Fe compositional sequence were essentially homogenous, suggesting a disequilibrium commonly used to indicate formation temperatures below

300°C [18]. However, a much more complete study (including analyses of a wider range of carbonate compositions) found something distinctly different; that there was a distinct correlation between O-isotope and major-element compositions [19]. While this correlation could not unambiguously distinguish between a high- or low-temperature of formation for the carbonates, it did show that isotopic compositions could be consistent with the impact metasomatism scenario for a small volume system.

**Other Observations and Conclusions:** Many of the loudest criticisms of the impact metasomatism hypothesis have focused on the notion that it required reaching equilibrium at high temperature, which would reset specific isotopic or physical systems to values other than those observed [e.g., 20]. Contrary to this assumption, H&M envisioned a rapid, nearly instantaneous event; reactions at elevated temperatures providing Ca, Mg and Fe to a  $\text{CO}_2$  fluid, which on further cooling producing the observed carbonates and associated phases. Unfortunately, without knowing the exact temperature, pressure, fluid composition and duration of the event, one can only explore the reactions supplying cations for the observed carbonates, rather than set strict limits on formation conditions. To use a common buzz-word, the proposed impact metasomatism is as much a “disequilibrium” process as any low-temperature precipitation mechanism, with one reaction supplying cations to a fluid that later deposits an oversaturated precipitate. Such reactions can be initiated either thermally or allochemically.

In summary, impact metasomatism still serves as a viable possible mechanism for carbonate formation in ALH 84001. Perhaps the biggest handicap of the impact metasomatism hypothesis has been its “alien” nature; i.e., it doesn’t seem familiar to those favoring Earth-like conditions on early Mars, and to paraphrase many, “it just doesn’t feel right.” But perhaps ALH 84001 carbonates should serve as a reminder that Mars is NOT Earth, and that processes such as impact metasomatism, which are almost certainly familiar to Mars, may require us to think “like a martian.”

**REFERENCES:** [1] Harvey & McSween (1996) *Nature* 382, 49. [2] McKay D., et al. (1996) *Science* 273, 924. [3] James P., et al. (1992) in *Mars* (U. Arizona Press), 934. [4] Martinez I., et al. (1994) *Earth Planet. Sci. Lett.* 121, 559. [5] Treiman A. (1995) *Meteoritics* 30, 294. [6] Kring D. et al. (1998) *Geochim. Cosmochim. Acta* 62, 2155. [7] Thomas-Keptra K. et al. (1997) *LPS XXVIII*, 1433. [8] Anovitz & Essene (1987) *J. Petrol.* 28, 389. [9] Mittlefehldt D. (1994) *Meteoritics* 29, 214. [10] Trommsdorff & Connolly (1990) *Contr. Miner. Petrol.* 104, [11] Johannes W. (1969) *Am. J. Sci.* 267, 1083. [12] Ohnmacht, W. (1974) *J. Petrol.* 15, 303. [13] Bradley J. et al. (1996) *Geochim. Cosmochim. Acta* 60, 5149-5155. [14] Bradley J. et al. (1998) *Meteorit. Planet. Sci.* 33, 765. [15] Wentworth & Gooding (1995) *Proc. Lunar Planet. Sci. Conf. XXVI*, 1489. [16] Wadhwa & Crozaz (1995) *LPS XXVI*, 1451. [17] Romanek et al. (1994) *Nature* 372, 655. [18] Valley J. et al. (1997) *Science* 275, 1633. [19] Leshin L. et al. (1998) *Geochim. Cosmochim. Acta* 62, 3. [20] Treiman & Romanek (1998) *Meteorit. Planet. Sci.* 33, 737.